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THE STRUCTURE OF NONSTOICHIOMETRIC COMPOUNDS IN LIQUID STATE

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The short range order of liquid Ni-In, Fe-Ge and Bi-Te alloys has been investigated by means of X-ray diffraction method. Compositions of melts fall in the range of intermediate phases that exist near chemical compounds Ni_2In , Fe_2Ge , $FeGe_3$ and Bi_2Te_3 . The structure factors obtained and the calculated radial distribution functions show that tendency to interaction of unlike atoms is major in the atomic arrangement and as a result short order exists within a wide concentration range.

KEY WORDS: Nonstoichiometry, structure factor, intermetallic compound.

1. INTRODUCTION

The aim of this paper is to investigate the structure of liquid alloys which are crystallized into intermediate phases with different width of homogeneity range. Binary systems of Bi-Te, Ni-In and Fe-Ge were chosen for structural investigations. The former shows the deviation from stoichiometry at the composition Bi_2Te_3 . Ni-In system exhibits two intermediate phases (ϵ and β). In the Fe-Ge system the intermediate phase exists from 31 to 40 at.% Ge at 1373 K. This kind of systems consists of the intermediate phases and stoichiometric chemical compounds which deviate from stoichiometry via formation of vacancies, antistructural positions or occupied holes in a crystalline cell. These vacancies or other defects can be ordered and this can significantly determine many physical properties in solid state. For liquid state, a systematic investigation in the range corresponding to intermediate phase is limited. It is known when the stoichiometric point is located in the homogeneity range, the singular point is pronounced on the isotherm dependencies of physical properties, of both in liquid and solid state^{1,2}. In connection with this we would like to determine whether the specific crystalline structure begins its forming in liquid state before crystallization. Fact, that nonstoichiometric compound A_xB_y has one of the sublattice defected, is a cause to ask whether the partial atomic distributions A-A, B-B for corresponding molten alloy are "defected" too.

2. EXPERIMENTAL

The X-ray diffraction study was carried out using a high temperature $\Theta-\Theta$ diffractometer with vertical goniometer. The investigation of melts was done with copper and cobalt $k\alpha$ -radiations monochromatized by graphite crystal. Scattering intensity was measured with accuracy better than 2%. Temperature was measured and stabilized with the accuracy of ± 2 K. For the calculating of Faber Ziman total structure factors the measured data were corrected taking into account polarization and incoherent scattering. The investigation was done at temperatures of about 5 K above the corresponding liquids temperature and at definite by higher temperatures.

3. RESULTS AND DISCUSSION

Phase diagrams of investigated alloys show the tendency to interaction of unlike atoms which is most pronounced in sharpness of liquidus for Bi-Te and Fe-Ge systems¹. As a result, one can observe the occurrence of stable chemical compounds which exist in some homogeneity range. It is widest in Fe-Ge and Ni-In systems and significantly less Bi-Te. Perhaps a really homogeneity range has some different width from the presented in known handbooks³⁻⁵, but the main features are unchanged.

In Figure 1 structure factors obtained for liquid Ni-In alloys containing from 28 to 42 at % In are presented. The temperature of measurements of these curves is 2 K above the corresponding liquidus point. As it can be seen from the figure,

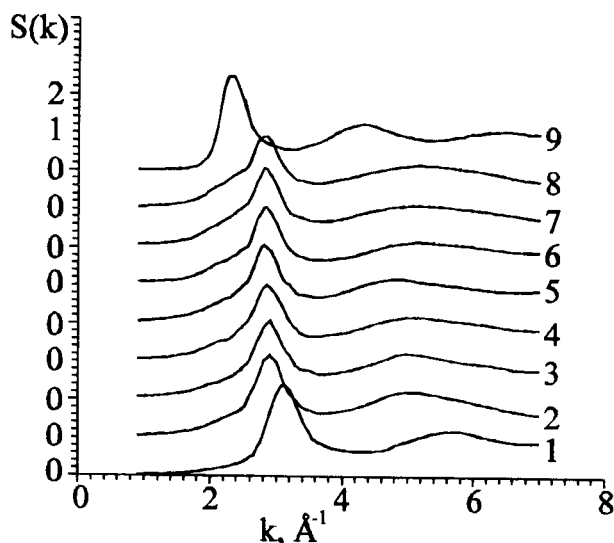


Figure 1 Concentration dependence of the structure factors for liquid Ni-In alloys: 1-0; 2-28; 3-31; 4-34; 5-36; 6-38; 7-40; 8-42, 9-100 at. % In.

the principal peak shows the untypical behaviour and on its left hand side, a small shoulder appears. The concentration dependence of the first maximum position is characterized by a positive deviation from the ideal behaviour which is typical for the systems with preferred interaction of unlike atoms. However, slight anomalous behaviour at about 36 at % In occurs and it is observed at higher temperatures, this behaviour may be not very clear. The second maxima of structure factors lies between those of pure indium and nickel. Thus, this maximum is less sensitive upon the addition of indium than the first one. The position of the second maximum position shows the growth when In is added and reaches the maximal point at about 40 at % In. This general characteristic exists, upon heating but at higher temperatures the second maximum position decreases when indium is added. In other words, at higher temperatures one can suggest that due to more intensive solution of atoms their distribution becomes closer to a statistically random structure.

Experimental structure factors were used for calculating the radial distribution function $g(r)$. Comparing the position of the main peaks for liquid alloys and components allows us to conclude that short range order is more similar to structure of Ni than In. But soluted In-atoms attempt to "remember" their own atomic arrangement and want to form it though at the beginning on the next neighbours and upon the heating in nearest coordination spheres.

Concentration dependence of the first coordination radius r_1 exhibits almost constant values in the range 29–42 at % In with a slight local increase at 36 at % In. This dependence shows that in investigated range of concentration structure is unchanged and topologically close to the structure of liquid Ni. When the temperature is above 50 K one can observe almost similar dependence but a tendency to increasing of r_1 takes place. Heating the melts up above 100 K leads to smooth increases of r_1 when indium is added and it is possible to consider these molten alloys as almost ideal solutions. Therefore, liquid alloys corresponding to intermediate ϵ -phase have an ordered structure which is topologically more close to the structure of Ni than of In and shows the chemical short range order in which atoms of In and Ni are coordinated in the way that is similar to a distorted cell of Ni_2In . Crucial to the behaviour of the structural parameters is the existence of the maximal chemical ordering not at the stoichiometric concentration but in the range of the liquidus line of the phase diagram.

Fe-Ge system is the system with two intermediate phases β and δ . The former in solid state has a Ni_2In type structure and, while the second – CuAl_2 type³. Chemical compounds Fe_2Ge and FeGe_2 are the basic alloys from which intermediate phases are formed. Alloys of these systems were investigated in⁶ by measuring electroconductivity and by means of X-ray method⁷. But composition of investigated melts was chosen with large step, and non-stoichiometric liquid alloys have not been investigated. Figure 2(a) shows the concentration dependence of the first maximum position k_1 at lowest temperature of investigation. As it can be seen from this figure the position of the main peak is closer to one of pure iron than germanium. In this dependence near the 36 at % Ge minimum occurs. For the nonstoichiometric FeGe_2 molten alloys one can observe high values of k_1 in the range 64–70 at % Ge and after that, abrupt decreasing and as

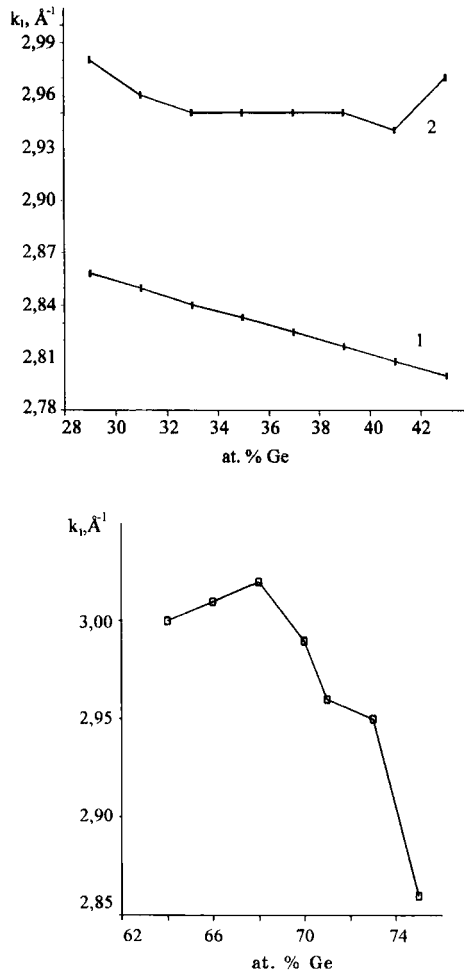


Figure 2 Concentration dependence of the first maximum position of $S(k)$ for liquid Fe-Ge alloys: (a) 29–43 at. % Ge, 1—calculated for statistical distribution of atoms, 2—experimental; (b) 64–75 at. % Ge.

result k_1 becomes close to germanium at its first maximum position (see Fig. 2(b)). Probably some increasing of k_1 at 66–68 at. % Ge is connected with most strong interaction of unlike atoms for stoichiometric FeGe_2 melt.

Hence liquid chemical compound Fe_2Ge is attempted to arrange atoms in close packed atomic structure with preference of metallic bonding and as a result this compound can solute atoms of Fe or Ge. In the case of FeGe_2 the structure is not as close as in Fe_2Ge , and atoms are preferentially covalently bonded. In this case topological short range order has many similarities with one of pure germanium.

The concentration interval short range order is most wide near molten Fe_2Ge (30–40 at. % In). When concentration begins to deviate from this interval increasing of first maximum position k_1 takes place. Observed deviation is not so large and can note that there are no significant changes in short range order.

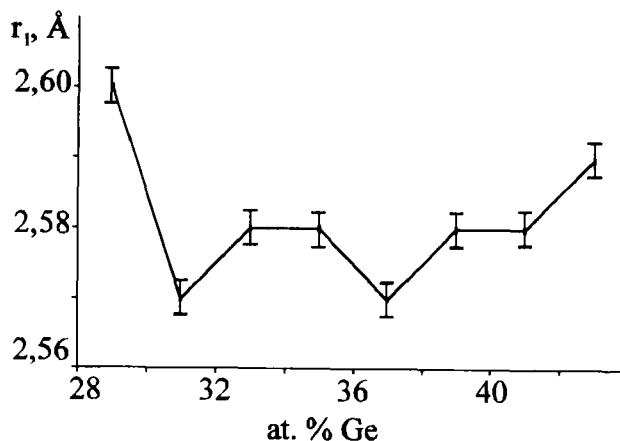


Figure 3 Concentration dependence of the most probable interatomic distance for liquid Fe-Ge alloys of 29–43 at. % Ge.

For an ideal solution estimated composition dependence of k_1 (line 1 in Fig. 2(a)) is significantly below the experimental curve that is evidence of preferred unlike atom interaction. But this dependence shows local wide minimum within 30–40 at.% Ge region where k_1 is constant. This fact shows that structure on the scale of nearest neighbours is the same at this concentration. In order words one can assume that in liquid state heterocoordinated structure exist near stoichiometry of Fe_2Ge . But shift of second maxima exhibits the more “defected” structure in next coordination shells.

The concentration dependence of the most probable interatomic distance is shown in Figure 3. As one can see r_1 is almost unchanged for all investigated alloys and very close to the corresponding value of pure iron. Thus, direct correlation between concentration dependencies of the first maximum position of structure factor and pair correlation function within the region of 30–40 at.% Ge is not observed. As is known the shift of $S(k)$ first maximum position to small value of k_1 is displayed by increasing of r_1 in $g(r)$ under condition that other peaks are unchanged. Consequently investigated alloys can not be considered as simple solutions of atoms.

Anomalous behaviour of $S(k)$ within the region of 29–43 at.% Ge does not lead to the significant changes in short range order because as we think chemically ordered microdomains A_xB_y can solute atoms of Fe or Ge remaining their structure without changes. Some Ge atoms which are covalently bonded form self associated complexes Ge_n but their influence on short range order shows no significant structural changes. Probably the coexistence of such two structural units is the reason of the fact that we have anomalous behaviour in concentration dependence of $S(k)$ and at the same time of the constant value of first interatomic distance within the range of 23–43 at.% Ge.

When alloys are more enriched by Ge that as in the case of alloys within 64–70 at.% Ge the number of self associated microdomains increases and as result significant structural changes take place. For these liquid alloys atomic arrangement has many similarities with the structure of liquid Ge.

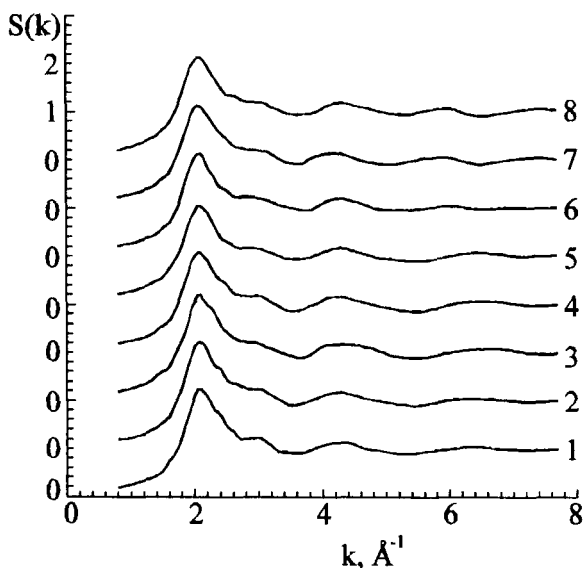


Figure 4 Structure factors for liquid Bi-Te alloys: 1–52; 2–55; 3–57; 4–59; 5–60; 6–61; 7–63; 8–65 at.% Te.

Thus for melts corresponding to nonstoichiometric alloys of δ -phase homogeneous structure within some concentration range is not observed.

The observed structure factors $S(k)$ of the Bi-Te alloys with composition in the 52–65 at.% Te are shown in Figure 4. The chemical compound Bi_2Te_3 falls into this interval of concentration and according to³ its homogeneity range is 52–65 at.% Te. Narrower homogeneity range can be seen in phase diagram presented in⁴; however the conclusion about its width in solid state cannot be considered as final.

As it can be seen from Figure 4, the experimental $S(k)$ has the asymmetrical first peak with a shoulder on the right hand side. A similar shoulder on the right hand side. A similar shoulder is the molten Bi. The position of the first peak is closer to the peak of Bi than Te. There is a small difference also between the second maxima. The height of the maxima is small and they have a flat form, especially at the right-hand side.

Significant broadening of the peaks may be caused by the influence of Te-like groups of atoms. The left-hand side of the principal peak of $S(k)$ has the small shoulder, which is located at $k = 1.5 \text{ \AA}^{-1}$. Its appearance can be attributed to existing of the intermediate-range order, which is also observed in glasses⁸.

The concentration dependence of the first peak position k_1 is displayed in Figure 5. In the range of 52–59 at.% Te k_1 is constant and with further adding of Te begins to increase. Thus, this dependence is characterized by anomalous behaviour near stoichiometric composition of Bi_2Te_3 . The first coordination radius decrease slowly and at 60 at.% Te begins to grow. This increasing of r_1 is significantly anomalous behaviour because the first interatomic distance for liquid Te is smaller than for Bi and consequently in suggestion of ideal mixture of atoms concentration

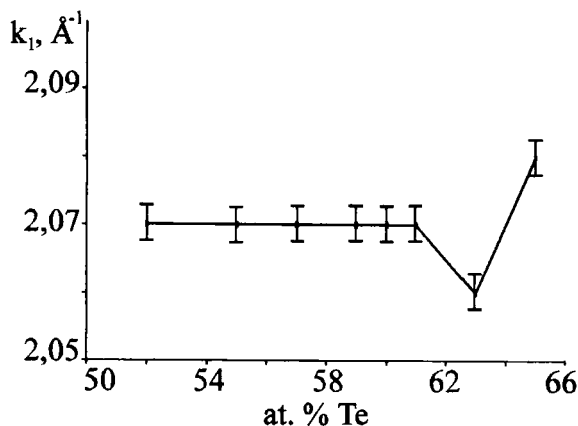


Figure 5 Concentration dependence of the first maximum position of $S(k)$ for liquid Bi-Te alloys.

dependence $r_1(c)$ should be decreasing when Te is added. Such local increasing of r_1 we consider as a result of nonsolubility of Te in Bi_2Te_3 complexes.

One can observe also the sharp increasing of the concentration dependence of coordination number of the first neighbour shell near the composition of 60 at.% Te. Using these experimental results, it seems possible to draw the conclusion that tendency to form compound in liquid state is most pronounced at 60 at.% when atoms of Te are added to liquid Bi_2Te_3 the atomic arrangement begins to change significantly. It is confirmed by concentration dependence of r_2/r_1 which is about 2.0 to Bi-enriched alloys and sharply decreases beginning from the Bi_2Te_3 stoichiometry. It must be noted the most metals show the r_1/r_1 ratio to be about 1.90. For alloys same value of r_2/r_1 occurs at 62 at.% Te and more. Thus, the concentration dependence of r_2/r_1 is characterized by an anomalous behaviour which exhibits the maximum in the range of 55–60 at.% Te. When analyzing other liquids, it can be seen that the maximum values of r_2/r_1 are observed in Si (2.28), Ge (2.06) and Zn (1.83), K (1.84), Cr (1.84). Taking into consideration the mentioned facts, it seems possible to conclude that the r_2/r_1 ratio is large for liquids with covalent bonds and minimal for close packed melts with metallic bonds. This allows us to suggest that investigated Bi-Te alloys are most covalently bounded in the range of 55–60 at.% Te. But covalent bonds coexist with the metallic ones, and as a result, the liquid Bi-Te alloys show more complicated structure comparing with the strong covalent liquids like Te and Se.

Analyzing the concentration dependence of the structural parameters it is possible to suggest that the strongest chemical interaction of unlike atoms occurs in the range 56–60 at.% Te. At the composition of 60 at.% Te short range order is determined by Bi_2Te_3 -like structure.

The addition of Te atoms promotes pronounced changes and displays different atomic arrangement of liquid Bi_2Te_3 and Te. Thus, the structure of liquid compound Bi_2Te_3 has the "homogeneity" range located to about 5 at.% to the left from stoichiometric point. When atoms of Te, which, according to the structural

investigation can form as covalently bounded groups, are added to stoichiometric liquid, the abrupt structural changes reveal. As we can see from the concentration dependence of coordination number, first maximum position of $g(r)$ and r_2/r_1 ratio extremal point in these dependencies are located near 63 at.% Te. We can, therefore, assume that atoms of Te cannot be substituted for atoms of Bi, as within the left-hand side region of concentration.

4. CONCLUSION

The structural investigation of liquid alloys containing components with different bondings between atoms and having nonstoichiometric range of concentration shows that topological structure is more similar to Ni, Fe and Bi than to In, Ge, Te correspondingly. This fact allows to conclude that influence of more metallic elements on the melt's structure is significantly strong. It is attribute not only 3d-transition elements (Fe, Co) but also of semimetal Bi. For all investigated systems preferring of unlike atoms, an interaction is observed. By adding more covalent atoms (In, Ge, Te) to stoichiometric compounds Ni_2In , $FeGe_2$ and Bi_2Te_3 the short range order becomes closer to the structure of these pure liquids. But we must note that this effect is less in intermediate phases formed by Ni_2In and Fe_2Ge than for ones based on the $FeGe_2$ and Bi_2Te_3 .

If we compare the concentration dependence of structure for intermediate phases in Ni-In, Fe-Ge and Bi-Te systems than it can be seen that concentration range of the ordered and microhomogeneous structure has wider range when second component is more metallic (Te-Ge-In). First component of these systems can easy be soluted in ordered structural groups and consequently we can observe the existence the Fe, Ni and Bi-like structure when those components are added to stoichiometric melt. In the case when more electronegative element is added the short range order varies significantly and forming of micrononhomogeneous structure takes place.

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